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(54) MANUFACTURE OF ORGANIC/METAL OXIDE COMPOSITE THIN FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To effectively form an organic/metal oxide composite thin film having an extremely thin metal oxide thin film and an organic compound thin film with satisfactory thickness accuracy.
SOLUTION: Metal compound having a group capable of generating hydroxyl group by condensation reacting solid hydroxyl group or carboxyl group and hydrolysis is brought into contact with a solid surface having a hydroxyl group or carboxyl group, and the metal compound is chemically adsorbed. Then, after excess metal compound is removed, the metal compound existing on the solid surface is hydrolyzed to form a metal oxide thin film. Further, organic compound capable of chemically adsorbing to the metal oxide thin film surface is brought into contact with the surface of the formed oxide thin film, and excess organic compound is removed.

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CLAIMS

[Claim(s)]
[Claim 1]Chemical absorption of these metallic compounds is carried out by contacting metallic compounds which have a basis which carries out a condensation reaction to a hydroxyl group of

this solid, or a carboxyl group, and can generate a hydroxyl group by hydrolysis to a solid surface which has a hydroxyl group or a carboxyl group, Subsequently, after removing superfluous metallic compounds, hydrolyze metallic compounds which exist in the above-mentioned solid surface, and a metal oxide thin film is made to form, After performing operation of making the above-mentioned metal oxide thin film forming on the surface of a metal oxide thin film formed if needed, once or more, A manufacturing method of the organicity/metal oxide composite thin film contacting an organic compound which can be chemisorbed on this metal oxide thin film surface on the surface of a metal oxide thin film which constitutes a surface layer, and making an organic compound film form in it by removing a superfluous organic compound.
[Claim 2]A manufacturing method of the organicity/metal oxide composite thin film of claim 1 as an organic compound, It carries out using that in which a hydroxyl group or a carboxyl group may exist on the organic compound film surface formed, A manufacturing method of the organicity/metal oxide composite thin film performing operation of making a metal oxide thin film in claim 1 forming on the organic compound film surface formed by that cause, once [at least] or more.
[Claim 3]On the surface of a metal oxide thin film which constitutes a surface layer of the organicity/metal oxide composite thin film formed in claim 2, A manufacturing method of the organicity/metal oxide composite thin film repeating by turns operation of making an organic compound film in claim 2 forming furthermore, and operation of performing operation of making a metal oxide thin film forming, once [at least] or more, performing them, and forming organicity/metal oxide composite thin film one by one.
[Claim 4]A manufacturing method of the organicity/the metal oxide composite thin film according to claim 3 carrying out so that a metal oxide thin film and one layer of organic compound films may be respectively formed at a time by turns.
[Claim 5]In the organicity/metal oxide composite thin film formed one by one, A manufacturing method of the organicity/the metal oxide composite thin film according to claim 3 forming at least one layer of a metal oxide thin film or an organic compound film with different metallic compounds or an organic compound from a metal oxide layer of other layers, or an organic compound film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the new method for manufacturing organicity/metal oxide composite thin film to a solid surface. It is a manufacturing method of the organicity/metal oxide composite thin film which can form often [thickness accuracy] and certainly detailed very thin organicity/metal oxide composite thin film.
[0002]
[Description of the Prior Art]It is strongly demanded of the composite material which comprises

an organic compound and a metallic oxide in dynamic, physical, and the field with the various development that can expect chemical property which are not in each material. Since it has the kinetic property with which the toughness of polymers and the integrity of the oxide were doubled, the composite material which consists of a high molecular compound and a metallic oxide is actually positioned as one of the vital-structures materials of today. The composite material of polymers and a metallic oxide is excellent in elasticity, abrasion resistance, and chemical stability.
It is expected as future tire and shield material.
It gropes for wide range application until it results in an optical element with a metallic oxide containing an organic molecule new from coloring of general-purpose material. The composite material mixed with the molecule and the atom level furthermore can serve as a substance group which shows the completely new characteristic which is not the former.
[0003]Many have a practical meaning only after the characteristic of such a composite material serves as a thin film. For example, although much more high integration of the electron device serves as an important technical target in today's semiconductor industry, for the purpose, the stable insulation film by which thickness control was carried out with the nano level is indispensable. In the precision electronic equipment which produces mechanical frictions, such as a hard disk, the thin film which has the characteristic of moderate softness and abrasion resistance which carries out glimpse repulsion is needed.
[0004]In the opto-electronics field it will be expected from now on that utilization is, it gropes for thin-layer-coating art with sufficient reflection efficiency, and development of the precise and uniform lamination type thin-film-fabrication process has been an important technical technical problem with the nano level. Especially in manufacture of an optical fiber or an optical waveguide, establishment of the thin-layer-coating art to a detailed and complicated-shaped base is made into pressing need. The compound thin film, as for, the organic molecule with large polarizability of coloring matter etc. carried out rule orientation serves as a big target when manufacturing an SHG element.
[0005]In the reverse osmotic membrane etc. which are used for the various demarcation membranes and desalting of a chemical, it is known that a surface structure of a super-thin layer will have big influence on the performance. In this case, it has been an important technical problem how the molecule and the atomic structure control of a diaphragm structure are realized.
[0006]Many attentions are attracted to the organicity/metal oxide composite thin film formed from a metal oxide thin film and an organic compound also as a means to reform the physics of a structural material or general-purpose products, and chemical property. It is thought [thermal, chemical, and] according to the thin layer coating to the plastic which needs transparency that grant of dynamic stability enables wide range application of a polymer material from glasses to the windshield of a car. Of course, in order to spread these widely socially, development of a cheap thin-film-fabrication process is considered to be an important breakthrough.
[0007]When the metallic oxide in a composite material is thin-film-ized to a quantum size field (several nanometers or less), the original energy state of a substance becomes discrete and realization of efficient energy conversion and electrochemical reaction of it is attained.
[0008]In the technical field of these many, the necessary condition common to the manufacturing process of a compound thin film is that a presentation and structure manufacture the thin film controlled by the nano level under cheaper and mild conditions. Simultaneously, dynamic, optical, chemical, thermal, and the thing that is the thin-film-fabrication processes which can design an electronic characteristic arbitrarily which are searched for is needed.
[0009]Conventionally, the following techniques are known as a method of manufacturing organicity/metal oxide composite thin film. For example, in a sol-gel method, water and an organic solvent are added if needed to the mixed solution of a metal alkoxide and an organic molecule, and a thin film several micrometers thick is obtained by dip or carrying out spin coating in this solution. However, since the thickness of a gel coating film is determined by hydrodynamic physical quantity, such as viscosity of a sol solution, and density, in this case, it is dramatically difficult to create a uniform thin film of 0.1 micrometer or less.

[0010]It is possible to produce organicity / metallic-oxide complex film on a solid board by making argillite, and hetero and isopoly ion adsorb [the organic high polymer electrolyte and by turns] which have an electric charge opposite to these. Free control of a diaphragm structure is possible by choosing an adsorption order and the number of times of adsorption in this method. However, the organic high polymer electrolyte and inorganic ion which can be used have a limitation, and, at present, it cannot become a large general method.

[0011]

[Problem(s) to be Solved by the Invention]At present, the manufacturing process of practical organicity/metal oxide composite thin film which can control thin and a presentation by a nano level is not found as above. The conditions needed for a new thin-film-fabrication process when the problem of the conventional thin-film-fabrication process is taken into consideration, The manufacturing process itself is a manufacturing process which can design a diaphragm structure so that it may be manufacturing a thin film with sufficient productivity by the precision of a nano level and a demand of still more various thin film characteristics can be satisfied at any time from a general precursor.

[0012]Then, by simple operation, it is flexible, and this invention is precise, and a mechanical design is possible and an object of this invention is to provide the manufacturing process of the organicity/metal oxide composite thin film of high intensity.

[0013]

[Means for Solving the Problem]This invention persons inquired wholeheartedly that an aforementioned problem should be solved. As a result, contact a metal alkoxide compound to a solid surface which has a hydroxyl group or a carboxyl group in excessive amount, and it is made to chemisorb, After removing a superfluous metal alkoxide compound which sticks to this solid surface physically, hydrolyze a metal alkoxide compound which exists in this solid surface, and it ranks second, By carrying out chemical absorption of the organic compound, and removing a superfluous organic compound by contacting this solid surface and an organic compound which can be chemisorbed, Since thickness of the organicity/metal oxide composite thin film formed is regulated by adsorption saturation of a metal alkoxide compound and an organic compound, That the organicity/metal oxide composite thin film of fixed thickness are formed, and by repeating this operation, In serial formation of the above-mentioned organicity/metal oxide composite thin film this organicity/metal oxide composite thin film can be formed with sufficient thickness accuracy one by one, By changing a metaled kind about metallic compounds to be used, it finds out that hybrid organicity/metal oxide composite thin film can be formed, and came to complete this invention.

[0014]To namely, a solid surface in which this invention has a hydroxyl group or a carboxyl group. By contacting metallic compounds which have a basis which carries out a condensation reaction to a hydroxyl group of this solid, or a carboxyl group, and can generate a hydroxyl group by hydrolysis, carry out chemical absorption of these metallic compounds, and it ranks second, After removing superfluous metallic compounds, hydrolyze metallic compounds which exist in the above-mentioned solid surface, and a metal oxide thin film is made to form, After performing operation of making the above-mentioned metal oxide thin film forming on the surface of a metal oxide thin film formed if needed, once or more, It is a manufacturing method of the organicity/metal oxide composite thin film contacting an organic compound which can be chemisorbed on this metal oxide thin film surface on the surface of a metal oxide thin film which constitutes a surface layer, and making an organic compound film form in it by removing a superfluous organic compound.

[0015]In a manufacturing method of organicity/metal oxide composite thin film according [this invention] to a described method, As an organic compound, it carries out using that in which a hydroxyl group or a carboxyl group may exist on the organic compound film surface formed, A manufacturing method of the organicity/metal oxide composite thin film performing operation of making a metal oxide thin film in a described method forming on the organic compound film surface formed by that cause, once [at least] or more is provided.

[0016]On the surface of a metal oxide thin film in which this invention constitutes a surface layer of the organicity/******************** formed in a described method, Operation of

making an organic compound film in a described method forming furthermore, and operation of performing operation of making a metal oxide thin film forming, once [at least] or more are repeated by turns, and are performed, and a manufacturing method of the organicity/metal oxide composite thin film forming organicity/metal oxide composite thin film one by one is also provided.

[0017]A manufacturing method of the organicity/metal oxide composite thin film carrying out this invention in a method of making the above-mentioned organicity/metal oxide composite thin film forming one by one so that a metal oxide thin film and one layer of organic compound films may be respectively formed at a time by turns is also provided.

[0018]And further in the organicity/metal oxide composite thin film in said method formed one by one this invention, A manufacturing method of the organicity/metal oxide composite thin film forming at least one layer of a metal oxide thin film or an organic compound film with different metallic compounds or an organic compound from a metal oxide layer of other layers or an organic compound film is also provided.

[0019]In a method of this invention, the organicity/metal oxide composite thin film in which thickness was controlled in several nanometers by solid surface can be formed by the above operation. It is presumed to be a thing based on the following principles that such a thin film is formed.

[0020]That is, first, if particles of metallic compounds and metal alkoxide gel which have an alkoxyl group, a hydroxyl group of a solid surface, and a solution of metallic compounds, such as a metal complex which can be chemisorbed, are made to immerse a solid which has a hydroxyl group or a carboxyl group on the surface, these metallic compounds will combine with a solid surface, and it will be adsorbed strongly. It not only chemisorbs metallic compounds with a solid surface, but in that case, it sticks to them superfluously as a weak physical-adsorption kind. If this is washed at suitable time and temperature, only a weak physical-adsorption kind will be washed and a thin film of thickness of a monad of chemisorbed metallic compounds will be formed in a solid surface. Next, if this solid is put into the air suitable in water of a suitable temperature which carries out time immersion or contained a steam, a molecule of metallic compounds which stuck to the surface will hydrolyze, a thin film of an oxide will be formed by condensing mutually, and a new hydroxyl group will be simultaneously formed in that surface. A reaction which air oxidation of the metal atom of metallic compounds is carried out simultaneously with hydrolysis, and forms a metallic oxide may also occur simultaneously.

[0021]Then, if a metal oxide thin film formed by doing in this way is made to immerse a solution of an organic compound which has a functional group which can be chemisorbed in this thin film surface, this organic compound will combine with the metal oxide thin film surface, and it will be adsorbed strongly. If this is washed at suitable time and temperature, only a weak physical-adsorption kind will be washed and a thin film of thickness of a monad of a chemisorbed organic compound will be formed in the metallic-oxide surface. When the above-mentioned thin film forming is carried out using an organic compound etc. which carry out two or more owners of a hydroxyl group or the carboxyl group, a hydroxyl group and a carboxyl group can be made to exist in the surface of the above-mentioned organic compound film formed. In such a case, it becomes possible again using a hydroxyl group and a carboxyl group on this surface of an organic compound film to make said metal oxide thin film form on it.

[0022]Organicity/metal oxide composite thin film can be made to form one by one by this invention by repeating such operation.

[0023]

[Embodiment of the Invention]In this invention, the solid in which a metal oxide thin film is made to form will not be restricted, especially if it has a hydroxyl group and a carboxyl group on the surface. For example, it is applicable to various solids, such as an organic matter, an inorganic substance, metal, etc. which have these bases on the surface. Metal, such as a solid which specifically consists of organic matters which consist of inorganic substances, such as glass, titanium oxide, and silica gel, such as a solid, polyacrylic acid, polyvinyl alcohol, cellulose, and phenol resin, iron which has the characteristic that the surface oxidizes easily, aluminum, and silicon, is typical.

[0024]When applying this invention to the solid which does not have a hydroxyl group in the surface, for example, a cadmium sulfide, poly aniline, gold, etc., the method of introducing a hydroxyl group or a carboxyl group is recommended to this solid surface. Introduction of a hydroxyl group is adopted that a publicly known method does not especially have restriction. For example, on the surface of gold, a hydroxyl group can be introduced by adsorption of mercaptoethanol etc.
[0025]The quantity of the hydroxyl group made to exist in the above-mentioned solid surface, or a carboxyl group, the case where it is going to form a good metal thin film in order to affect the density of the metal oxide thin film formed -- general -- the $5.0\times10^{13} - 5.0\times10^{14}$ equivalent /cm^2 -- the range of the $1.0\times10^{14} - 2.0\times10^{14}$ equivalent / cm^2 is suitable preferably.
[0026]Solid shape and a surface state in particular are not restricted. That is, since it is based on making the method of this invention chemisorb by contacting metallic compounds to a solid surface, it does not need to be smooth and this surface can choose various things also as construction material or shape.
[0027]The shape of the solid which can apply this invention, and a size are various from the solid surface of various gestalten, such as fibrous, the shape of a bead, powder, and a thin film integrated circuit, or the inner surface of the wall and filter of a tube, or porous material to the thing of the large area of a wall etc.
[0028]In this invention, the publicly known compound which has a basis which carries out the condensation reaction of the metallic compounds to the hydroxyl group of a solid surface or a carboxyl group, and can generate a hydroxyl group by hydrolysis is especially used without restriction. If typical metallic compounds are illustrated, titanium butoxide ($Ti(O\text{-}nBu)_4$), Zirconium propoxide ($Zr(O\text{-}nPr)_4$), aluminum butoxide ($aluminum(O\text{-}nBu)_3$), Metal alkoxide compounds, such as niobium butoxide ($Nb(O\text{-}nBu)_5$); Methyl trimetoxysilane ($MeSi(O\text{-}Me)_3$), Diethyldiethoxysilane ($Et_2Si(O\text{-}Et)_2$) etc., The metal alkoxide which has two or more alkoxyl groups; metal alkoxides, such as double alkoxide compound [, such as metal alkoxide;$BaTi(OR)_X$ which have ligands, such as an acetylacetone, and has two or more alkoxyl groups,];, are mentioned.
[0029]In this invention, a small amount of water is added to this metal alkoxide other than the above-mentioned metal alkoxides, The particles of the alkoxide gel produced by making hydrolyze and condense selectively, A titanium butoxide tetramer ($C_4H_9O[Ti(OC_4H_9)_2O]_4C_4H_9$) etc., It is also possible to use the polymers based on two cores which have two or more sorts of metallic elements two or more or the alkoxide compound of a cluster type, and the metal alkoxide compound which constructed the bridge over one dimension via the oxygen atom, etc.
[0030]It is possible to also use a metal complex which chemisorbs with the hydroxyl group of a solid surface and produces a new hydroxyl group on the surface by hydrolysis etc. in this invention as said metallic compounds. As the above-mentioned metal complex, specifically Metal halogenides, such as a cobalt chloride ($CoCl_2$), Metal carbonyl compounds, such as titanium oxo acetyl acetate ($TiO(acac)_2$) and pentacarbonyliron ($Fe(CO)_5$), and these polynuclear clusters can also be used.
[0031]The metallic compounds of this invention can also form a multiple oxide thin film in a solid surface by using it combining two or more sorts if needed.
[0032]In this invention, the contact with metallic compounds and a solid is adopted that the contact method which makes these metallic compounds stick to this solid surface by saturated adsorption does not especially have restriction. The method of immersing a solid in the solution made to dissolve metallic compounds in an organic solvent generally, or applying this solution to a solid surface by methods, such as a spin coat, is preferred. The above-mentioned solvent in particular is not restricted. For example, generally, it is independent in methanol, ethanol, propanol, toluene, a carbon tetrachloride, benzene, etc., or the case of metal alkoxides can mix and use these.
[0033]About 10-100 mM is preferred for the concentration of the metallic compounds in the

above-mentioned solution.
[0034]They are the time for 3 to 20 minutes, and what is necessary is just to determine them within the limits of room temperature -50 ** generally, although contact time and the temperature cannot change with adsorptive activities of the metallic compounds to be used and cannot generally be limited.
[0035]It is also possible again in the case of the above-mentioned chemical absorption to shorten time required for these processes substantially by using catalysts, such as acid and a base.
[0036]By the above-mentioned operation, the metallic compounds of saturated adsorption and the superfluous metallic compounds by physical adsorption exist in a solid surface to the hydroxyl group or carboxyl group of the surface.
[0037]In this invention, there are important requirements in removing the metallic compounds which stick to the overabove. That is, since a metal oxide thin film is formed of the layer of the metallic compounds chemisorbed in a solid surface by removing the metallic compounds which exist superfluously, based on the abundance of these metallic compounds, a metal oxide thin film can be formed with very sufficient accuracy with high reproducibility.
[0038]The removing method of metallic compounds with the superfluous above will not be restricted especially if it is the method of removing these metallic compounds selectively. For example, the method of washing with said organic solvent is preferred. The method of carrying out soak cleaning of the washing to this organic solvent, the method of carrying out spray washing, the method of carrying out steam cleaning, etc. are adopted suitably. Temperature [in / in washing temperature / said contact operation] is adopted suitably.
[0039]In this invention, hydrolysis is performed after washing of the above-mentioned superfluous metallic compounds. These metallic compounds condense and a metal oxide thin film is formed by this hydrolysis.
[0040]The above-mentioned hydrolysis is adopted that a publicly known method does not especially have restriction. For example, operation in which the solid to which metallic compounds were made to stick is immersed in water is the most common. In order to prevent mixing of an impurity etc. and to generate the metallic oxide of a high grade as this water, ion exchange water is preferred. In hydrolysis, it is also possible by using catalysts, such as acid and a base, to shorten time required for these processes substantially.
[0041]However, what has reactivity high among metallic compounds with water can also be hydrolyzed at reacting to the water vapor of the air.
[0042]After hydrolysis, as occasion demands, the surface is dried by the gas for desiccation, such as nitrogen gas, and the metal oxide thin film of this invention is obtained.
[0043]In this invention, adjustment of the thickness of the metal oxide thin film formed can be carried out on a nano meter level by repeating a series of above operations once or more, and performing them.
[0044]That is, adjustment of the thickness of a metal oxide thin film is attained by repeating removal of the chemical absorption by contact with metallic compounds, and superfluous metallic compounds, and operation of hydrolysis once or more, and performing them using the hydroxyl group which exists in the metal oxide thin film formed by hydrolysis.
[0045]Next, in this invention, this thin film surface and the organic compound which can be chemisorbed are contacted on the surface of the metal oxide thin film formed by the above operation. The above-mentioned chemical absorption is based on chemical bonds, such as a coordinate bond and a covalent bond, and this sticks to an organic compound firmly, without being removed from a metal oxide thin film, even if it presents the same operation as the removing method of the above mentioned superfluous metallic compounds. It is not restricted, the adsorption etc. which carry out a condensation reaction to the hydroxyl group which exists in the adsorption produced when oxygen atoms, such as a hydroxyl group and a carboxyl group, coordinate to the metal atom of a metallic oxide, for example, or a metal oxide thin film, and are produced mention, and especially such chemical absorption is ****. Although an usable organic compound is not limited in this invention, what has two or more hydroxyl groups or carboxyl groups from a viewpoint which adsorption produces more firmly, and is in solid description under

a room temperature (25 **) is preferred. Therefore, polysaccharide, such as high molecular compound; starch, glycogen, etc. which have hydroxyl groups and carboxyl groups, such as polyacrylic acid, polyvinyl alcohol, polymethacrylic acid, and polyglutamic acid, as an organic compound; disaccharides, such as glucose and mannose, monosaccharide, etc. are used preferably.

[0046]In this invention, the contact method of above mentioned metallic compounds and solid and the same method can adopt the contact with the above-mentioned organic compound and a metal oxide thin film without restriction. The method of generally immersing a solid in the solution made to dissolve an organic compound in polar solvents, such as water or ethanol, is preferred. The concentration of the organic compound in the above-mentioned solution is preferred in about 1-10mg/ml. Contact time and temperature are the time for 5 to 20 minutes, and what is necessary is just to determine them within the limits of room temperature -50 ** generally.

[0047]And in this invention, a superfluous organic compound is removed like the case of contact of the above mentioned metallic compounds. Thereby, an organic compound film is formed of the layer of the organic compound chemisorbed on the metal oxide thin film surface. This can form an organic compound film with very sufficient accuracy with high reproducibility based on the abundance of this organic compound. The removing method of the above mentioned metallic compounds and the same method can adopt the removing method of the organic compound in that case without restriction. The method of washing with the solvent of the organic compound especially described above is preferred. Temperature [in / in washing temperature / said contact operation] is adopted suitably.

[0048]The organicity/metal oxide composite thin film in which the metal oxide thin film and the organic compound film were laminated can be made to form in a solid surface by the above. After forming this organic compound film, a hydroxyl group and a carboxyl group can be made to still exist in this thin film surface here, when what carries out two or more owners of the hydroxyl group and carboxyl group like said illustrated compound is used as an organic compound. Therefore, a metal oxide thin film can be made to form in the surface by the still more nearly same operation as the above by this invention in such a case using the hydroxyl group and carboxyl group on this surface of an organic compound film. And it is still more possible to also make an organic compound film form on the surface, and the organicity/metal oxide composite thin film of the multilayer structure which consists of various kinds, a metal oxide thin film of thickness, and an organic compound film can be made to form one by one by repeating such operation. Intensity becomes the extremely outstanding thing and especially the compound thin film obtained by carrying out so that a metal oxide thin film and one layer of organic compound films may be respectively formed at a time by turns has it. [preferred]

[0049]By repetition of such a process, a tens of [several to] nanometers compound thin film can be formed with sufficient accuracy by this invention. Here, when the metal alkoxide which has a metal atom of pieces, such as titanium butoxide, is used for formation of a metal oxide thin film, a thin film several angstroms thick can be laminated one by one according to adsorption conditions. In this case, the increase in the thickness per 1 cycle supports adsorption of the monomolecular layer of a metal alkoxide. On the other hand, if the particles of alkoxide gel, etc. are used, a thin film about 60 nanometers per 1 cycle thick can also be laminated. On the other hand, when polyacrylic acid is used as an organic polymer compound, a thin film several angstroms thick can be formed according to adsorption conditions. In this invention, the thin film of the accuracy of the above-mentioned thickness can be suitably manufactured according to the grade of serial lamination of the above-mentioned metal oxide thin film layer and an organic compound film layer.

[0050]In that case, by changing the kind of metallic compounds and the organic compound to be used, it is hybrid lamination and it is possible to obtain the layered product of a compound thin film.

[0051]Thus, the main features and the industrial use of the manufactured organicity/metal oxide thin film are as follows.

[0052]since this invention can manufacture very uniformly the organicity/metal oxide composite

thin film of a NANOMETORU field, it serves as important base art which boils and twists a next-generation high integration device. It can use as the production technology of the highly precise insulation film in an electronics field, and production technology of the efficient reflection coat film in the opto-electronics field, and, specifically, can expect to be applied also to manufacture of a minute magnetic storage element etc.

[0053]This invention is easy operation under a mild condition, and can expect to be able to manufacture organicity/metal oxide composite thin film to the surface of all shape, or the substrate of a large area, and to spread widely as coating technique of general-purpose products, since productivity is high. Specifically, it can use for grant of various surface-protection films of a plastic, the antibacterial coat of medical science or foodstuffs allied products, the static-free film of clothes or an electric product, the antioxidant film of apparatus with complicated shape, and scientific and dynamic stability to a structural material, etc.

[0054]Since organicity/metal oxide composite thin film is manufactured for a short time by a very simple technique [say / contacting a solid to metallic compounds and an organic compound], the method of this invention does not need special equipment, but can expect high productivity.

[0055]Even if the method of this invention is based on the saturation adsorption by a solid surface and does not set up strictly the temperature in the concentration of metallic compounds or an organic compound, washing, and hydrolysis, time, etc., it can manufacture organicity/metal oxide thin film precise enough.

[0056]Since the method of this invention can laminate various organicity/metal oxide composite thin films in the accuracy of NANOMETORU, it can design a new electrical-and-electric-equipment and electronic characteristic, magnetic characteristic, and light functional characteristic in itself. Specifically, it can use for manufacture of semiconductor superlattice material, and the design of an efficient photochemical reaction or electrochemical reaction. Since [remarkable] it is low as compared with the technique of others [manufacturing cost / of organicity/metal oxide composite thin film], this invention can serve as practical base art, such as light energy conversion system, such as a solar cell.

[0057]According to the method of this invention, since organicity/metal oxide composite thin film can be created in a bead or the particle surface, it becomes possible to change these dynamic and physicochemical characteristics a lot. Dynamic and the physicochemical stability of these can be remarkably improved by manufacturing organicity/metal oxide composite thin film to the inner surface of porous material or a hollow filament.

[0058]According to the method of this invention, since a presentation and laminated structure of organicity/metal oxide composite thin film can be designed, it can use for manufacture of the demarcation membrane of various substances, or a reverse osmotic membrane. It becomes possible to manufacture various functionally gradient materials by changing gradually the lamination ratio of two or more kinds of metallic compounds. By combining with the serial adsorption process of the organic compound proposed from the former, the design of a super-thin film [various type / organicity and inorganic composite] is also attained, and a new light, an electron, and the super-thin film that has the function can be manufactured. [many]

[0059]

[Effect of the Invention]As mentioned above, as explained in detail, in this invention, it is mild conditioning and easy operation, and the compound thin film which consists of the uniform oxide film and organic compound film of a NANOMETORU field can be manufactured on the surface of all shape, or the substrate of a large area. This invention can manufacture the organicity/metal oxide composite thin film of the high intensity which has various laminated structures, and the productivity is also very high. The method of this invention of having the feature without a parallel other than these, as various coating technique of general-purpose products as important base art which boils and twists a next-generation high integration device, As a means to manufacture the thin film material which has a new electrical-and-electric-equipment, electronic characteristic, magnetic characteristic, and light functional characteristic, As a means to reform the physicochemical characteristics of a solid surface, it is expectable to be applied to various kinds of fields as a means to design organicity and an inorganic compound super-thin film

material various type, and to manufacture as a means to design various isolation films as a means to build an efficient catalyst system, and to manufacture.
[0060]
[Example]Hereafter, although an example explains this invention in more detail, this invention is not limited to these examples.
[0061]In order that an oxide film might show one by one that it is laminated in the constant rate by the method of example 1 this invention, the oxide film to the crystal oscillator top was created. A crystal oscillator is a device which can measure the weight of the thin film which was known as microbalance and formed on the surface from the frequency change in the accuracy of 10^{-9}g.
[0062]After the crystal oscillator's having immersed for 12 hours what was covered with the gold electrode in the ethanol solution of the mercaptoethanol of 10mM and introducing a hydroxyl group into the surface, what sprayed nitrogen gas and was fully dried after washing by ethanol was used.
[0063]As Example 1, in the solution of the titanium butoxide ($Ti(O-nBu)_4$) of 100mM melted into 1:1 mixed solvents of toluene and ethanol. The crystal oscillator which introduced the hydroxyl group into the surface with the described method is made immersed for 3 minutes at 30 **, it ranks second and is immersed in 30 ** ethanol for 1 minute, and nitrogen gas is sprayed and it was made to have been immersed in 30 ** ion exchange water for 1 minute, to have made the metal oxide thin film form, and to dry after washing. In subsequently, 10mg/ml of polyacrylic acid solution melted in ethanol. The organic compound film was made to form in the surface of this metal oxide thin film by making the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface immersed for 10 minutes at 30 **, being immersed in 30 more ** ethanol for 1 minute, spraying nitrogen gas and making it dry after washing. It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.
[0064]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 1 was shown in Table 1.
[0065]
[Table 1]

表 1

	-ΔF (Hz)
0	0
Ti	61
PAA	124
Ti	202
PAA	247
Ti	329
PAA	363
Ti	448
PAA	514
Ti	612
PAA	680
Ti	750
PAA	811
Ti	912
PAA	1000
Ti	1079
PAA	1143
Ti	1216
PAA	1284
Ti	1384
PAA	1455

[0066]The frequency change of this example was made into the graph, and it was shown in drawing 1. As shown in drawing 1, the pitch of the crystal oscillator was decreasing in proportion to the number of lamination cycles. This result shows that the metal oxide thin film and organic compound film of fixed weight are formed in the electrode surface of a crystal oscillator one by one by the method of this invention.
[0067]Next, the XPS spectrum of the organicity/metal oxide composite thin film obtained above was measured, and the elementary composition near [which was estimated from the result] the surface was shown in Table 2.
[0068]
[Table 2]

表 2

	Ti−PAA 複合薄膜		
元素	Ti	C	O
元素組成比	1.0	9.7	6.0

[0069]The composition ratio of carbon and oxygen was mostly in agreement with polyacrylic acid independent composition ratio. This result shows that the surrounding donor atom of ligand of a titanium atom is limited to the oxygen atom of the carboxyl group origin of polyacrylic acid. It was thought from the composition ratio of titanium and carbon that about 3 times as many acrylic acid units existed to the titanium atom in a compound thin film.
[0070]The reflective infrared absorption spectrum of this organicity/metal oxide composite thin film was measured. The result was shown as drawing 2. The strong absorption near 1560 cm^{-1} and 1720 cm^{-1} belongs to the C=O stretching vibration of the carboxyl group of polyacrylic acid configurated with the titanium atom, respectively, and the carboxyl group which has not been configurated with a titanium atom. These results show that the carboxyl group which is not participating in coordination exists in that polyacrylic acid / titanium oxide compound thin film pushes, and is formed in the coordination of the carboxyl group to a titanium atom, and a

polyacrylic acid thin film.
[0071]When the section of this organicity/metal oxide composite thin film was observed with the scanning electron microscope, as shown in the photography image of drawing 3, the compound thin film of uniform and fixed thickness was formed. The density of the compound thin film calculated from the thickness measured from this photography image and a crystal oscillator was 1.8g/cm^3. This value is larger than the density (1.66g/cm^3) of dry gel and the density (1.41g/cm^3) of polyacrylic acid which were created from titanium butoxide by the usual method. It was checked that the polyacrylic acid / titanium oxide compound thin film manufactured by the method of this invention have packing structure more precise than each constituent by this.
[0072]When adsorption weight (W) and the increase of stock of the thickness of the compound thin film in the forming face product (S) of a thin film to each lamination cycle were calculated based on the density of this compound thin film, the increase of stock of the thickness of the compound thin film in each lamination cycle was about 2 nanometers. The average frequency changes after adsorption of the adsorption back of titanium butoxide and polyacrylic acid are 87 Hz and 68 Hz, respectively.
The increase in the thickness per 1 cycle has been divided into about 1-nanometer titanium oxide layer and the polyacrylic acid layer, respectively.

[0073]Not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator. Not separating at all, even if this compound thin film performs boiling for 10 minutes in hot water and immersion for 10 minutes in the inside of the alkaline aqueous solution of pH 11, or ultrasonic-cleaning operation (30W, 38 kHz) for 10 minutes was checked.
[0074]Make the solution of the titanium butoxide of 100mM melted into 1:1 mixed solvents of example 2 toluene and ethanol immerse the crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 for 3 minutes at 30 **, and it ranks second to it, Are immersed in 30 ** ethanol for 1 minute, it is immersed in 30 ** ion exchange water for 1 minute, and a metal oxide thin film is made to form after washing, and nitrogen gas was sprayed and it was made to dry. Subsequently, a 5mg/ml PVA solution is made to immerse the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface for 10 minutes at 30 **, the organic compound film was made to form in the surface of this metal oxide thin film by resembling 30 more ** ion exchange water, being immersed for 1 minute, spraying nitrogen gas and making it dry after washing It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.
[0075]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 2 was shown in Table 3.
[0076]
[Table 3]

表 3

	・Δ F (Hz)
0	0
Ti	42
PVA	134
Ti	219
PVA	352
Ti	432
PVA	557
Ti	689
PVA	829
Ti	910
PVA	1065
Ti	1171
PVA	1336
Ti	1417
PVA	1591
Ti	1672
PVA	1832
Ti	1929
PVA	2104
Ti	2227
PVA	2397

[0077]The frequency change of this example was made into the graph, and it was shown in drawing 4.
[0078]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0079]Make the solution of the titanium butoxide of 100mM melted into 1:1 mixed solvents of example 3 toluene and ethanol immerse the crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 for 3 minutes at 30 **, and it ranks second to it, Are immersed in 30 ** ethanol for 1 minute, it is immersed in 30 ** ion exchange water for 1 minute, and a metal oxide thin film is made to form after washing, and nitrogen gas was sprayed and it was made to dry. Subsequently, 1mg/ml of starch solution is made to immerse the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface for 10 minutes at 40 **, the organic compound film was made to form in the surface of this metal oxide thin film by resembling 40 more ** ion exchange water, being immersed for 1 minute, spraying nitrogen gas and making it dry after washing It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.
[0080]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 3 was shown in Table 4.
[0081]
[Table 4]

表 4

	-Δ F (Hz)		-Δ F (Hz)
0	0	Ti	831
Ti	34	Starch	873
Starch	69	Ti	920
Ti	109	Starch	966
Starch	140	Ti	1027
Ti	190	Starch	1067
Starch	219	Ti	1107
Ti	288	Starch	1148
Starch	324	Ti	1198
Ti	360	Starch	1243
Starch	386	Ti	1281
Ti	427	Starch	1320
Starch	458	Ti	1359
Ti	514	Starch	1399
Starch	553	Ti	1454
Ti	603	Starch	1504
Starch	639	Ti	1554
Ti	689	Starch	1606
Starch	724	Ti	1665
Ti	760	Starch	1718
Starch	800		

[0082]The frequency change of these examples was made into the graph, and it was shown in drawing 5.
[0083]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0084]Make the solution of the titanium butoxide of 100mM melted into 1:1 mixed solvents of example 4 toluene and ethanol immerse the crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 for 3 minutes at 30 **, and it ranks second to it, Are immersed in 30 ** ethanol for 1 minute, it is immersed in 30 ** ion exchange water for 1 minute, and a metal oxide thin film is made to form after washing, and nitrogen gas was sprayed and it was made to dry. Subsequently, the glucose solution of 100mM is made to immerse the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface for 10 minutes at 40 **, The organic compound film was made to form in the surface of this metal oxide thin film by being immersed in 40 more ** ion exchange water for 1 minute, spraying nitrogen gas and making it dry after washing. The above thin-film-forming operation was repeated 5 times by turns, and was performed, and organicity/metal oxide composite thin film was laminated one by one. Then, toluene, the solution of the titanium butoxide ($Ti(O-nBu)_4$) of 100mM melted into 1:1 mixed solvents of ethanol, and the malt sugar solution of 100mM are used, The same thin-film-forming operation was repeated 5 times by turns, and was performed, and organicity/metal oxide composite thin film was laminated further one by one.
[0085]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 4 was shown in Table 5.
[0086]
[Table 5]

表 5

	-ΔF (Hz)
0	0
Ti	66
Glu	91
Ti	165
Glu	209
Ti	306
Glu	399
Ti	480
Glu	558
Ti	596
Glu	653
Ti	734
Mal	766
Ti	820
Mal	891
Ti	959
Mal	1072
Ti	1143
Mal	1252
Ti	1322
Mal	1454

[0087]The frequency change of this example was made into the graph, and it was shown in drawing 6.
[0088]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0089]The average frequency change of the crystal oscillator in the above Examples 1-4 was shown in Table 6.
[0090]
[Table 6]

表 6

実施例	有機化合物 (濃度)	溶媒 (温度・吸着時間)	平均振動数変化	
			有機化合物	チタン
1	PAA (10 mg/ml)	エタノール (30℃、10分)	67.8 Hz	86.8 Hz
2	PVA (5 mg/ml)	水 (30℃、10分)	148.8 Hz	90.9 Hz
3	デンプン (1 mg/ml)	水 (40℃、10分)	67.8 Hz	71.8 Hz
4	グルコース (100 mM)	水 (40℃、20分)	59.4 Hz	71.2 Hz
	マルトース (100 mM)	水 (40℃、20分)	91.4 Hz	68.8 Hz

[0091]In the solution of the aluminum butoxide (aluminum(O-nBu) $_3$) of 10mM melted into 2:1 mixed solvents of example 5 toluene and 1-butanol. Make the crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 immersed for 10 minutes at 45 **, and it ranks second, After being immersed in 2:1 mixed solvents of 45 ** toluene and ethanol for 1 minute, washing and rinsing by ethanol further, it is immersed in 45 ** ion exchange water for 1 minute, and a metal oxide thin film is made to form, and nitrogen gas was sprayed

and it was made to dry. In subsequently, 10mg/ml of polyacrylic acid solution melted into ion exchange water. The organic compound film was made to form in the surface of this metal oxide thin film by making the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface immersed for 10 minutes at 30 **, being immersed in 30 more ** ion exchange water for 1 minute, spraying nitrogen gas and making it dry after washing. It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.

[0092]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 5 was shown in Table 7.

[0093]

[Table 7]

表 7

	-Δ F (Hz)
0	0
Al	66
PAA	152
Al	236
PAA	289
Al	457
PAA	522
Al	619
PAA	686
Al	807
PAA	873
Al	997
PAA	1047
Al	1194
PAA	1235
Al	1331
PAA	1398
Al	1531
PAA	1590
Al	1758
PAA	1798

[0094]The frequency change of this example was made into the graph, and it was shown in drawing 7.

[0095]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.

[0096]Make the solution of the zirconium propoxide ($Zr(O\text{-}nPr)_4$) of 107mM melted in example 61-propanol immerse the crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 for 5 minutes at 30 **, and it ranks second to it, After being immersed in 30 ** 1-propanol for 1 minute and washing, it is immersed in 30 ** ion exchange water for 1 minute, and a metal oxide thin film is made to form, and nitrogen gas was sprayed and it was made to dry. In subsequently, 10mg/ml of polyacrylic acid solution melted in ethanol. The organic compound film was made to form in the surface of this metal oxide thin film by making the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface immersed for 10 minutes at 30 **, being immersed in 30 more ** ethanol for 1 minute, spraying nitrogen gas and making it dry after washing. It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.

[0097]The frequency change (**F) of the crystal oscillator based on lamination of the

organicity/metal oxide composite thin film of Example 6 was shown in Table 8.
[0098]
[Table 8]
表 8

	-ΔF (Hz)
0	0
Zr	47
PAA	98
Zr	175
PAA	227
Zr	288
PAA	345
Zr	455
PAA	512
Zr	653
PAA	722
Zr	832
PAA	891
Zr	987
PAA	1057
Zr	1186
PAA	1265
Zr	1350
PAA	1433
Zr	1539
PAA	1646
Zr	1749
PAA	1869

[0099]The frequency change of this example was made into the graph, and it was shown in drawing 8.
[0100]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0101]Make the solution of the zirconium propoxide ($Zr(O-nPr)_4$) of 107mM melted in example 71-propanol immerse the crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 for 5 minutes at 30 **, and it ranks second to it, After being immersed in 30 ** 1-propanol for 1 minute and washing, it is immersed in 30 ** ion exchange water for 1 minute, and a metal oxide thin film is made to form, and nitrogen gas was sprayed and it was made to dry. Subsequently, a 5mg/ml PVA solution is made to immerse the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface for 10 minutes at 30 **, The organic compound film was made to form in the surface of this metal oxide thin film by being immersed in 30 more ** ion exchange water for 1 minute, spraying nitrogen gas and making it dry after washing. It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.
[0102]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 7 was shown in Table 9.
[0103]
[Table 9]

表 9

	-ΔF (Hz)
0	0
Zr	81
PVA	138
Zr	221
PVA	249
Zr	331
PVA	370
Zr	449
PVA	490
Zr	577
PVA	633
Zr	717
PVA	761
Zr	844
PVA	892
Zr	987
PVA	1063
Zr	1123
PVA	1171
Zr	1250
PVA	1294

[0104]The frequency change of this example was made into the graph, and it was shown in drawing 9.
[0105]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0106]Make the solution of the zirconium propoxide ($Zr(O-nPr)_4$) of 100mM melted in example 81-propanol immerse the crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 for 5 minutes at 30 **, and it ranks second to it, After being immersed in 30 ** 1-propanol for 1 minute and washing, it is immersed in 30 ** ion exchange water for 1 minute, and a metal oxide thin film is made to form, and nitrogen gas was sprayed and it was made to dry. Subsequently, 1mg/ml of starch solution is made to immerse the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface for 10 minutes at 40 **, The organic compound film was made to form in the surface of this metal oxide thin film by being immersed in 40 more ** ion exchange water for 1 minute, spraying nitrogen gas and making it dry after washing. It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.
[0107]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 8 was shown in Table 10.
[0108]
[Table 10]

表１０

	-ΔF (Hz)		-ΔF (Hz)
0	0	Zr	1376
Zr	34	Starch	1441
Starch	98	Zr	1502
Zr	157	Starch	1560
Starch	222	Zr	1645
Zr	291	Starch	1724
Starch	352	Zr	1812
Zr	419	Starch	1895
Starch	486	Zr	1972
Zr	554	Starch	2027
Starch	618	Zr	2087
Zr	685	Starch	2152
Starch	755	Zr	2242
Zr	817	Starch	2317
Starch	881	Zr	2391
Zr	975	Starch	2464
Starch	1049	Zr	2547
Zr	1136	Starch	2610
Starch	1196	Zr	2711
Zr	1268	Starch	2792
Starch	1338		

[0109]The frequency change of this example was made into the graph, and it was shown in drawing 10.
[0110]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0111]In the solution of the titanium barium double alkoxide (BaTi (OR) $_X$) of 10mM melted into 1:1 mixed solvents of example 9 toluene and ethanol. The crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 is made immersed for 5 minutes at 30 **, and it ranks second, and after being immersed in 30 ** ethanol for 1 minute and washing, nitrogen gas was sprayed and it was made for it to be immersed in 30 ** ion exchange water for 1 minute, and to make a metal oxide thin film form, and to dry. In subsequently, 10mg/ml of polyacrylic acid solution melted in ethanol. The organic compound film was made to form in the surface of this metal oxide thin film by making the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface immersed for 5 minutes at 30 **, being immersed in 30 more ** ethanol for 1 minute, spraying nitrogen gas and making it dry after washing. It carried out by having repeated the above thin-film-forming operation, and organicity/metal oxide composite thin film was laminated one by one.
[0112]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 9 was shown in Table 11.
[0113]
[Table 11]

表１１

	-ΔF (Hz)
0	0
BaTi	134
PAA	186
BaTi	348
PAA	402
BaTi	585
PAA	630
BaTi	786
PAA	829
BaTi	1008
PAA	1040
BaTi	1198
PAA	1238
BaTi	1426
PAA	1460
BaTi	1641
PAA	1708
BaTi	1878
PAA	1940
BaTi	2041
PAA	2091

[0114]The frequency change of this example was made into the graph, and it was shown in drawing 11.
[0115]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0116]The average frequency change of the crystal oscillator in the above Examples 5-9 was shown in Table 12.
[0117]
[Table 12]

表１２

実施例	金属アルコキシド（濃度）／有機化合物（濃度）	溶媒（温度・吸着時間）	平均振動数変化
5	$Al(O\text{-}nBu)_3$ (10 mM)	トルエン／1-ブタノール＝2／1（45℃、10分）	121.5 Hz
	PAA (10 mg/ml)	水（室温、10分）	54.7 Hz
6	$Zr(O\text{-}nPr)_4$ (107 mM)	1-プロパノール（室温、5分）	96.7 Hz
	PAA (10 mg/ml)	エタノール（室温、10分）	73.2 Hz
7	$Zr(O\text{-}nPr)_4$ (107 mM)	1-プロパノール（室温、5分）	75.7 Hz
	PVA (5 mg/ml)	水（室温、10分）	53.7 Hz
8	$Zr(O\text{-}nPr)_4$ (100 mM)	1-プロパノール（室温、3分）	71.8 Hz
	デンプン (1 mg/ml)	水（40℃、10分）	67.8 Hz
9	BaTi ダブルアルコキシド (10 mM)	トルエン／エタノール＝1／1（室温、5分）	160.7 Hz
	PAA (10 mg/ml)	エタノール（室温、5分）	48.4 Hz

[0118]In the solution of the titanium butoxide ($Ti(O\text{-}nBu)_4$) of 100mM melted into 1:1 mixed solvents of example 10 toluene and ethanol. The crystal oscillator which introduced the hydroxyl group into the surface by the same method as Example 1 is made immersed for 3 minutes at 30 **, and it ranks second, and after being immersed in 30 ** ethanol for 1 minute and washing, nitrogen gas was sprayed and it was made for it to be immersed in 30 ** ion exchange water for 1 minute, and to make a metal oxide thin film form, and to dry. In subsequently, 10mg/ml of polyacrylic acid solution melted in ethanol. The organic compound film was made to form in the surface of this metal oxide thin film by making the crystal oscillator in which the metal oxide thin film was formed in the above-mentioned surface immersed for 10 minutes at 30 **, being immersed in 30 more ** ethanol for 1 minute, spraying nitrogen gas and making it dry after washing. The above thin-film-forming operation was repeated 5 times respectively by turns, and was performed, and organicity/metal oxide composite thin film was laminated one by one. Then, toluene, the solution (immersion during 10 minutes) of the aluminum butoxide ($aluminum(O\text{-}nBu)_3$) of 10mM melted in 2:1 mixed solvents of 1-butanol, and 10mg/ml of polyacrylic acid solution melted in ethanol are used, The same thin-film-forming operation was repeated 3 times by turns, and was performed, and organicity/metal oxide composite thin film was laminated further one by one.

[0119]The frequency change (**F) of the crystal oscillator based on lamination of the organicity/metal oxide composite thin film of Example 10 was shown in Table 13.

[0120]

[Table 13]

表１３

	-ΔF (Hz)
0	0
Ti	22
PAA	96
Ti	170
PAA	241
Ti	307
PAA	400
Ti	482
PAA	598
Ti	688
PAA	806
Al	895
PAA	960
Al	1086
PAA	1177
Al	1342
PAA	1446

[0121]The frequency change of this example was made into the graph, and it was shown in drawing 12.
[0122]Furthermore, not separating at all, even if it wears out strongly this organicity/metal oxide composite thin film in the surface with a brush was checked by the frequency change of the crystal oscillator.
[0123]Each example shown above forms the compound thin film on the metal surface embellished with mercaptoethanol.
[0124]However, this invention is not limited to the surface of metal which has a hydroxyl group on the surface by ornamentation. For example, it is already proven also from the ability to laminate one by one on various metallic-oxide surfaces in an example that the method of this invention is applicable to various metallic-oxide surfaces. It is checked independently that an oxide film as shown in the example can be manufactured also on the surface of the organic high polymer which has a hydroxyl group like polyvinyl alcohol, or the organic high polymer which has a carboxyl group. In especially the method of this invention on the basis of chemical adsorption with the hydroxyl group of a solid surface, and a carboxyl group, it is clear that there is no restriction in solid shape.

[Translation done.]

* NOTICES *

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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 1.
[Drawing 2]It is a figure showing the reflective infrared absorption spectrum of the compound thin film of Example 1.
[Drawing 3]It is a figure showing the photography image by the scanning electron microscope of the section of the compound thin film of Example 1.
[Drawing 4]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 2.
[Drawing 5]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 3.
[Drawing 6]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 4.
[Drawing 7]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 5.
[Drawing 8]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 6.
[Drawing 9]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 7.
[Drawing 10]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 8.
[Drawing 11]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 9.
[Drawing 12]It is a figure showing the frequency change of a crystal oscillator based on lamination of the compound thin film of Example 10.

[Translation done.]

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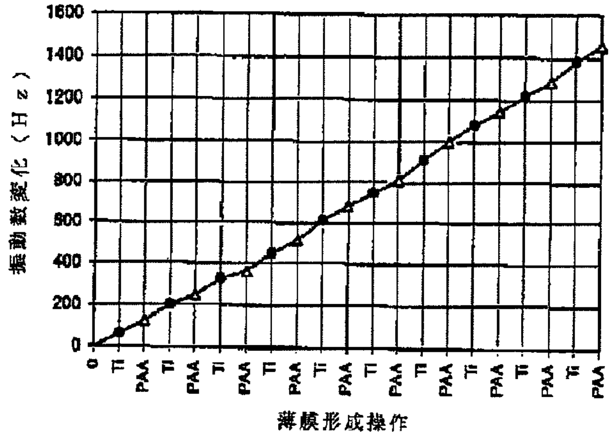
DRAWINGS

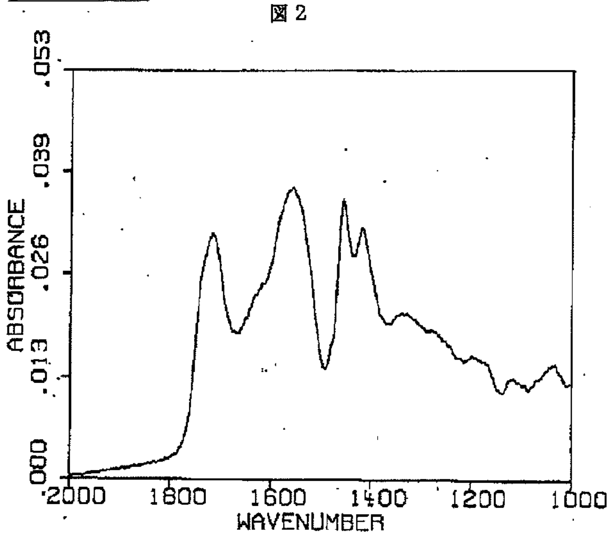
[Drawing 1]

図 1



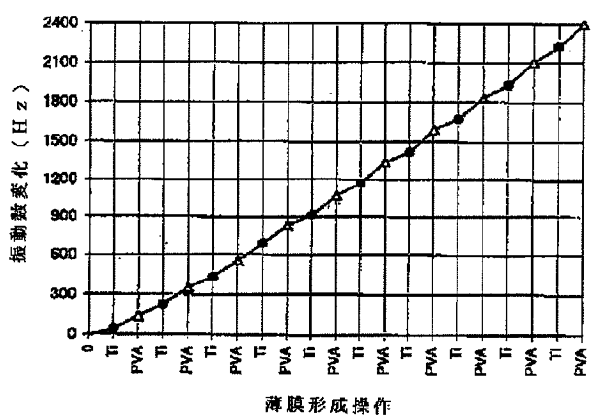
[Drawing 2]

図 2



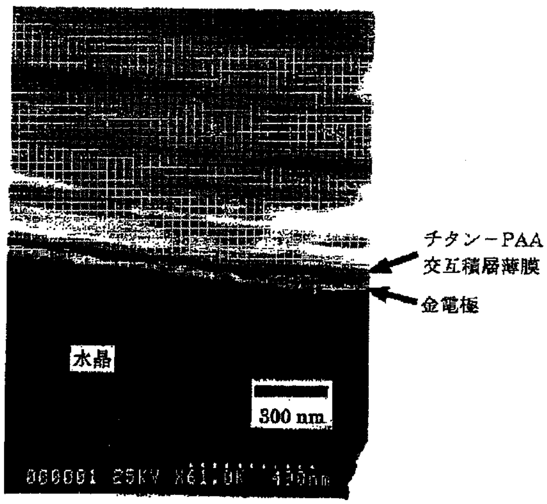
[Drawing 4]

図 4



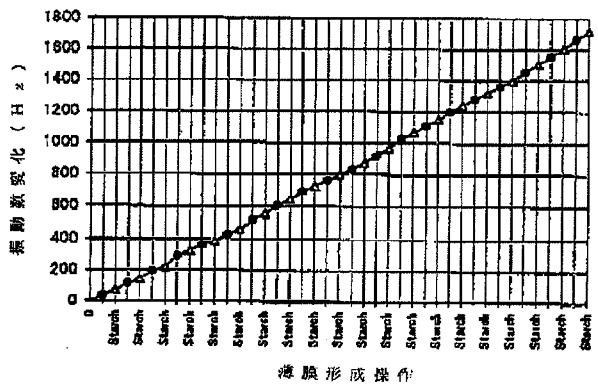
[Drawing 3]

図 3



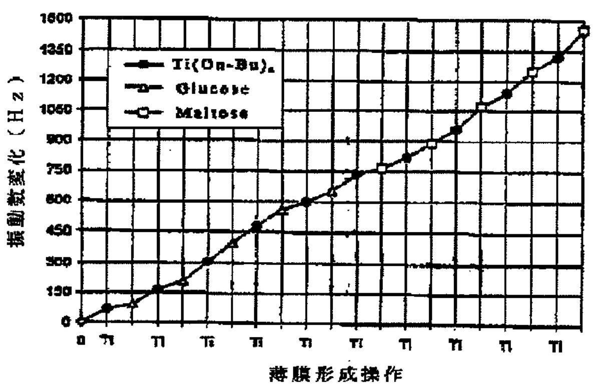
[Drawing 5]

図 5



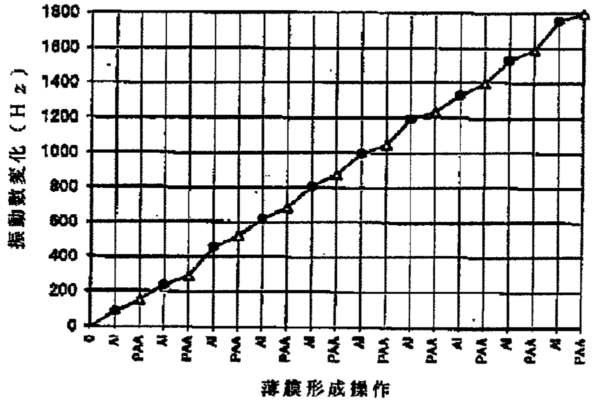
[Drawing 6]

図 6



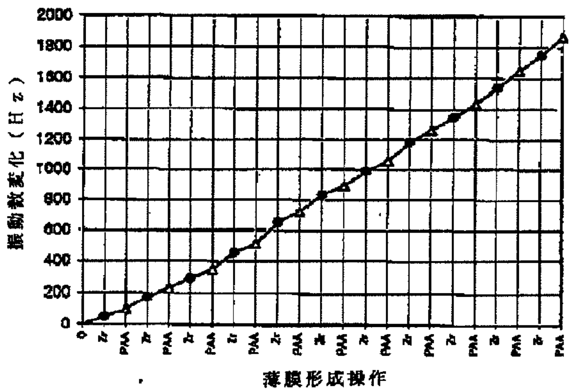
[Drawing 7]

図7



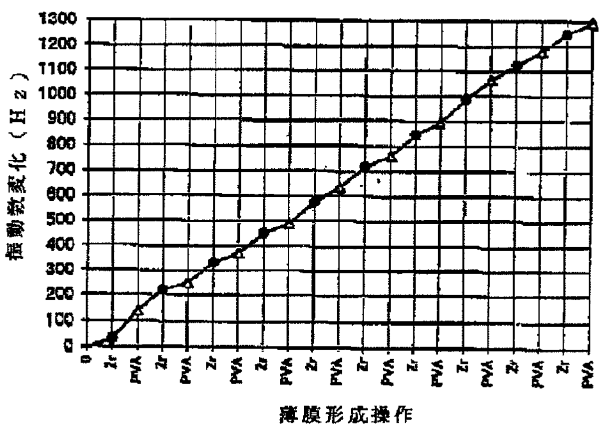
[Drawing 8]

図8



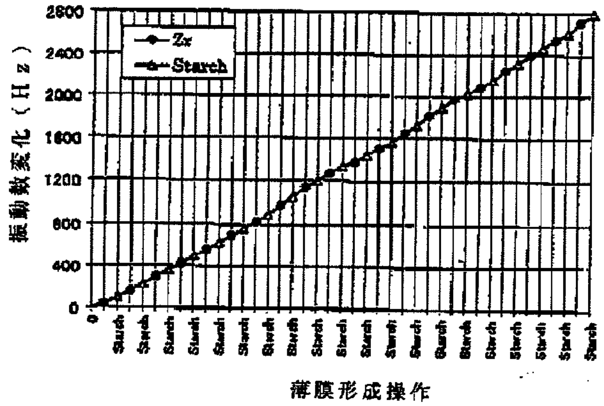
[Drawing 9]

図9



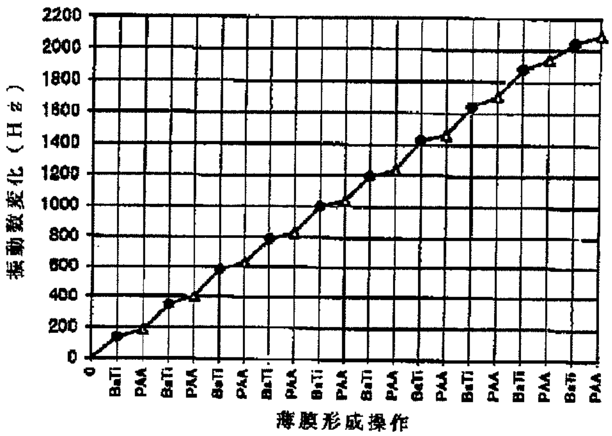
[Drawing 10]

図１０



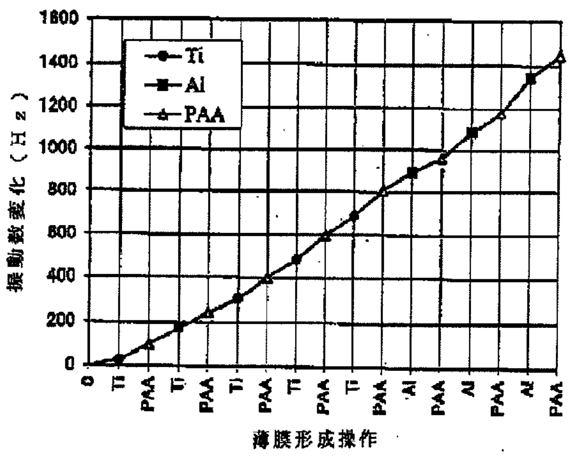
[Drawing 11]

図１１



[Drawing 12]

図１２



[Translation done.]